# Generation of Neutral CCCCBO in the Gas Phase from [CCCCBO]$^-$ and Rearrangement of Energized CCCCBO to OCCCCB: A Joint Experimental and Theoretical Investigation

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One-electron vertical Franck−Condon oxidation of [CCCCBO]$^-$ (using $O_2$ as collision gas in the dual collision cell region of an HF-ZAB/AMD 604 four-sector mass spectrometer) forms doublet neutrals $C_4BO$ in the first stage of a neutralization−reionization ($^-NR^+$) experiment. Reionization of these neutrals to decomposing positive ions shows that the majority of neutrals (formed in the first collision cell) correspond to CCCCBO which are stable for the microsecond duration of the NR experiment. However, a minor fraction of neutrals CCCCBO is energized and rearranges to form an isomer which decomposes by loss of CO. A theoretical study of this system at the MP4SDTQ/aug-cc-pVDZ//MP2(full)/6-31G(d) level of theory suggests that the rearranged species corresponds to OCCCCB. The rearrangement occurs by six-center cyclization of CCCCBO, involving O−C(1) bond formation followed by B−O bond cleavage to form OCCCCB. The reaction is endothermic by only 4.5 kcal mol$^{-1}$ but requires an excess energy of ≥ 53.5 kcal mol$^{-1}$ in order for the system to surmount the first transition state. This energy requirement is 45.5 kcal mol$^{-1}$ more than the Franck−Condon excess energy of 8 kcal mol$^{-1}$ of CCCCBO produced by the vertical oxidation process. The additional energy may be provided by keV collisions of CCCCBO with the collision gas $O_2$ following Franck−Condon-controlled neutralization of [CCCCBO]$^-$.

## 1. Introduction

Cumulenes and cumulene oxides have been studied in great detail because of their importance in flame chemistry and astrochemistry.[1] In contrast, studies of borocumulenes have been concentrated mainly on borocumulenes with boron occupying a terminal position in such molecules.[2] A number of species containing B, C, and O have also been reported including BCO, $B(CO)_2$ and $(CBO)_2$,[3−6] $C_{2n}BO^-$ [($n = 1−5$); no data concerning the structures are available],[3] and OCBBCO, a species which is reported[7] to possess triple bond BB character.

Our approach to the generation of transient neutrals in a mass spectrometer is to use collision-induced vertical oxidation of mass-selected anions of known bond connectivity by means of the neutralization−reionization (NR) procedure.[8−10] In this respect it is of prime importance that the anions are formed from precursors with well-defined, known structures (e.g., ref 11).

In a previous study,[2] we showed that stable anion [CCBO]$^-$ may be formed in the chemical ionization source of a mass spectrometer by the process $F^- + (CH_3)_3Si{-}C{\equiv}C{-}B(O{-}isoPr)_2 \rightarrow [CCBO]^- + (CH_3)_3SiF + isoPrOH + CH_3{-}CH{=}CH_2$. The anion [CCBO]$^-$ was then converted to doublet CCBO by a collision-induced vertical Franck−Condon oxidation in the first of two collision cells. Calculations at the MP4SDTQ/aug-cc-pVDZ//MP2(full)/6-31G(d) level of theory indicated that [CCBO]$^-$ and CCBO are linear species, with structures approximated by the valence bond forms [:C=C=B=O]$^-$ and ·C≡C−B=O, respectively. Neutral CCBO is stable at least for the microsecond duration of the neutralization experiment; there is no evidence of either decomposition or rearrangement of this neutral. Neutral CCBO may be converted to [CCBO]$^+$ in the second collision cell by vertical ionization. Some of the [CCBO]$^+$ cations are stable, while others are energized and undergo rearrangement to [OCCB]$^+$. This exothermic rearrangement may occur for both the singlet and triplet forms of [CCBO]$^+$ (the triplet form is lower in energy by only 5.2 kcal mol$^{-1}$) with both rearrangements proceeding through distorted rhombic forms of [*cyclo*-CCBO]$^+$.

This paper reports the results of a study of the neutral doublet system of CCCCBO. Several questions are addressed, namely, (i) can CCCCBO be formed by a process analogous to that used for CCBO, (ii) is CCCCBO stable (like CCBO) during or directly following the neutralization step of the gas-phase synthesis, or does CCCCBO have sufficient excess energy to effect decomposition or rearrangement (e.g., to OCCCCB), and (iii) if energized CCCCBO does rearrange, what is the mechanism of this rearrangement?

## 2. Experimental Section

**2.A. Mass Spectrometric Methods.** The experiments were performed using a modified HF-ZAB/AMD 604 four-sector mass spectrometer with BEBE configuration,[11] where B and E represent magnetic and electric sectors, respectively. The [CCCCBO]$^-$ anion was generated by chemical ionization (CI) in the negative ion mode, with typical source conditions as follows: source temperature 200 °C, repeller voltage −0.5 V, ion extraction voltage 8 kV, mass resolution $m/\Delta m \geq 1500$. $(CH_3)_3Si{-}(C{\equiv}C)_2{-}B(O{-}isoPr)_2$ was placed in a small glass capillary tube which was then drawn out in a flame to create a very fine aperture, allowing for a slow steady release of sample vapor upon heating. The capillary was inserted into the CI source via the direct probe; the probe tip was heated to 60−80 °C to generate a background pressure of about $10^{-5}$ Torr inside the source housing. The [CCCCBO]$^-$ anion was formed following

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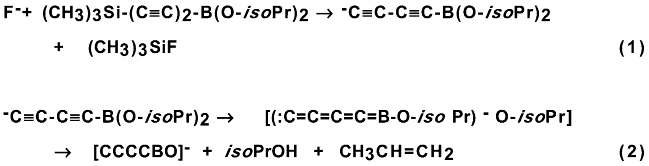
**SCHEME 1**



desilylation using the DePuy gas-phase $S_N2(Si)$ process[12] (followed by fragmentation as shown in Scheme 1) utilizing $SF_6$ as a CI reagent gas at a pressure of about $10^{-4}$ Torr inside the source housing.

Collision-induced dissociation (CID) of B(1)-mass-selected ions was effected in the second of the collision cells positioned between B(1) and E(1). Helium was used as a target gas. The pressure of the collision gas in the cell was maintained such that 80% of the parent ion beam was transmitted through the cell. This corresponds to an average of 1.1−1.2 collisions per ion.[13] Product ions resulting from CID were recorded by scanning E(1).

Neutralization−reionization ($^-NR^+$) experiments[8−10] were performed for B(1)-mass-selected $[CCCCBO]^-$ utilizing the dual collision cells located between sectors B(1) and E(1). Neutralization of the anions was achieved by collisional electron detachment using $O_2$ at 80% transmittance as collision gas, while reionization to cations was achieved by collision of the neutrals with $O_2$, again at 80% transmittance. Any ions remaining after the first collision event were deflected from the primary neutral beam using an electrode maintained at 1 kV positioned before the second collision cell. To detect a recovery signal due to the reionized parent molecule, the neutral species must be stable for approximately one microsecond. Charge reversal ($^-CR^+$) spectra[14,15] were recorded near single collision conditions ($O_2$, 80%T). Collection of $^-CR^+$ and $^-NR^+$ spectra under the same experimental conditions allows for a direct comparison from which it is possible to infer the behavior of the intermediate neutral on the NR time scale ($10^{-6}$ s).[9,16,17]

**2.B. Synthesis.** *2.B.1. (4-Trimethylsilylbutadiynyl)diisopropoxyborane*. To bis(trimethylsilyl)butadiyne (1.0 g, 5.2 mmol) in anhydrous diethyl ether (30 $cm^3$) at 20 °C under nitrogen was added methyl lithium/lithium bromide complex in diethyl ether (1.5 M, 4.0 $cm^3$, 6.0 mmol), and the mixture allowed to stir for 16 h at 20 °C. This organolithium reagent was then slowly added to triisopropyl borate (1.4 $cm^3$, 6.1 mmol) in diethyl ether (20 $cm^3$) at −78 °C, and the reaction mixture was maintained at −78 °C for 4 h. Anhydrous hydrogen chloride in diethyl ether (2.0M, 3.0 $cm^3$, 6.0 mmol) was added, and the mixture was allowed to warm to 20 °C. The precipitate was removed, and the remaining solvent was removed in vacuo. Any remaining triisopropyl borate and triisopropyl alcohol were removed by distillation at 90 °C/12 mbar, to give 0.6 g of raw product (46% yield). Attempts to further purify the compound led to decomposition. Mass spectrometric experiments were carried out on samples which were >95% pure by NMR. $^1H$ NMR (200 MHz, in $CDCl_3$): $\delta$ 0.20 (s, 9H), 1.12 (d, 2 × 6H, $J = 6.2$ Hz), 4.55 (septet, 2 × 1H, $J = 6.2$ Hz).

**2.C. Theoretical Methods.** All geometry optimizations were carried out at the MP2(full)/6-31G(d) level of theory using the GAUSSIAN 98 suite of programs.[20] Stationary points were characterized as either minima (no imaginary frequencies) or transition structures (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies which were then scaled by 0.9661[21] and used as a zero-point correction for the electronic energies calculated at higher levels of theory. The energies of these geometries were determined in single-point calculations at the MP4SDTQ level using the Dunning aug-cc-pVDZ basis set.[22,23] All calculations were carried out on the Alpha server at the APAC National Facility (Canberra).

**TABLE 1: Energies and Geometries of the $[CCCCBO]^-$ Anion**

| | singlet | triplet |
|---|---|---|
| energy (hartrees) | −251.825 142 | −251.649 053 |
| state | $^1\Sigma$ | $^3A'$ |
| C(1)C(2) (Å) | 1.275 | 1.235 |
| C(2)C(3) (Å) | 1.345 | 1.340 |
| C(3)C(4) (Å) | 1.253 | 1.234 |
| C(4)B (Å) | 1.445 | 1.442 |
| BO (Å) | 1.237 | 1.244 |
| C(1)C(2)C(3) (deg) | | 180.0 |
| C(2)C(3)C(4) (deg) | | 179.8 |
| C(3)C(4)B (deg) | | 176.6 |
| C(4)BO (deg) | | 179.8 |

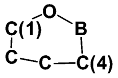
## 3. Results and Discussion

**3.A. Conversion of $[CCCCBO]^-$ to CCCCBO.** The required $[CCCCBO]^-$ precursor anion was generated in the ion source of the mass spectrometer by the process shown in Scheme 1. The CID spectrum of this anion (*m*/*z* 75) shows a weak fragment peak at *m*/*z* 48 (loss of neutral BO), consistent with the anion connectivity CCCCBO. Calculations at the MP4SDTQ/aug-cc-pVDZ//MP2(full)/6-31G(d) level of theory indicate that there are stable singlet and triplet forms of $[CCCCBO]^-$. Relevant details of these structures are recorded in Table 1. The singlet anion corresponds to the ground state, 110.5 kcal $mol^{-1}$ below the triplet. The linear singlet structure is best represented by the valence bond formulation $[:C{=}C{=}C{=}C{=}B{=}O]^-$, with the extra electron involved in the multiple bonding to boron. Details of the structure of the stable doublet neutral molecule are listed in Table 2: this structure is best represented by the valence bond formula $[\cdot C{\equiv}C{-}C{\equiv}C{-}B{=}O]$. The adiabatic electron affinity of CCCCBO is calculated to be 5.8 eV (cf. 4.8 eV for CCBO).[2] One-electron vertical oxidation of singlet $[CCCCBO]^-$ will initially give a neutral with the same geometry as the anion. This species has an excess Franck−Condon energy of 8 kcal $mol^{-1}$ above doublet CCCCBO on the neutral potential surface. This excess energy by itself should not be sufficient to cause major rearrangement or decomposition of CCCCBO following formation from $[CCCCBO]^-$. The data outlined above suggest that vertical one-electron oxidation of $[CCCCBO]^-$ should be a suitable method for the formation of stable CCCCBO.

The charge reversal ($^-CR^+$) and neutralization−reionization ($^-NR^+$) spectra of $[CCCCBO]^-$ are shown in Figure 1. The $^-NR^+$ spectrum is dominated by a parent (recovery) signal at *m*/*z* 75, indicating that the parent neutral(s) is (are) stable for the microsecond lifetime of the neutral(s) before reionization. A number of fragment ions observed in both $^-NR^+$ and $^-CR^+$ spectra are consistent with a connectivity CCCCBO, for example, those formed by losses of C, O, $C_2$, BO, CBO, $C_4$, $C_2BO$, and $C_3BO$. However, there are a number of peaks in both spectra which are not consistent with a structure CCCCBO. These are formed by losses of CO, $C_2O$, $C_3O$, and $C_4O$ from a parent cation which must have a C−O bond, for example, the structure $[OCCCCB]^+$.

So far, this story is comparable to that reported earlier for CCBO,[2] but that similarity now ends. In the case of CCBO,

**TABLE 2: Geometries and Energies of Stable $C_4BO$ Neutral Isomers**

| | C(1)C(2)C(3)C(4)BO **1** | C(1)C(2)BC(3)C(4)O **2** | C(1)BC(2)C(3)C(4)O **3** | BC(1)C(2)C(3)C(4)O **4** |  **5** |
|---|---|---|---|---|---|
| state | $^2\Sigma$ | $^2\Sigma$ | $^2\Sigma$ | $^2\Sigma$ | $^2A'$ |
| symmetry | $C_{\infty v}$ | $C_{\infty v}$ | $C_{\infty v}$ | $C_{\infty v}$ | $C_s$ |
| relative energy (kcal mol$^{-1}$)[a] | 0.0 | 7.6 | 50.9 | 4.5 | 39.9 |
| C(1)C(2) (Å) | 1.173 | 1.183 | | 1.283 | 1.300 |
| C(2)C(3) (Å) | 1.408 | | 1.273 | 1.278 | 1.360 |
| C(3)C(4) (Å) | 1.173 | 1.293 | 1.295 | 1.288 | 1.305 |
| C(4)B (Å) | 1.491 | | | | 1.415 |
| C(1)B (Å) | | | 1.382 | 1.354 | |
| C(2)B (Å) | | 1.493 | 1.411 | | |
| C(3)B (Å) | | 1.338 | | | |
| BO (Å) | 1.218 | | | | 1.362 |
| CO (Å) | | 1.176 | 1.177 | 1.175 | 1.393 |
| C(1)C(2)C(3) (deg) | | | | | 94.8 |
| C(2)C(3)C(4) (deg) | | | | | 164.4 |
| C(3)C(4)B) (deg) | | | | | 78.2 |
| C(4)BO) (deg) | | | | | 149.9 |

[a] Energies relative to neutral **1** (−251.611 593 hartrees).

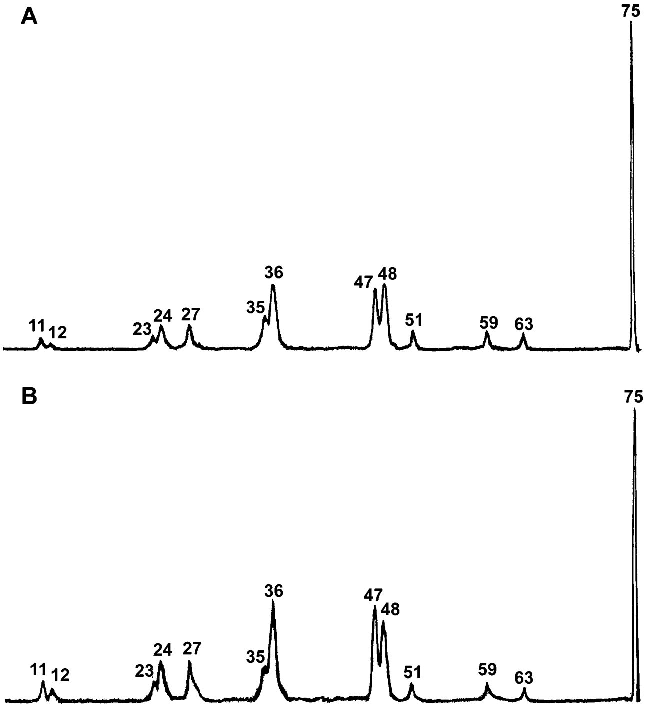


**Figure 1.** (a) $^-$CR$^+$ mass spectrum of [CCCCBO]$^-$. (b) $^-$NR$^+$ mass spectrum of [CCCCBO]$^-$. The experiments were performed using a HF-ZAB/AMD 604 four-sector mass spectrometer.

**TABLE 3: Energies of Selected Neutral and Cation Dissociations[a]**

| parent connectivity | fragment species | energy (kcal mol$^{-1}$) |
|---|---|---|
| CCCCBO | CCCC + BO | 29.8 |
| | CCC + CBO | 110.8 |
| | CC+ CCBO | 148.1 |
| CCCCBO$^+$ | CCCC$^+$ + BO | 98.6 |
| | CCCC + BO$^+$ | 80.8 |
| | CCC$^+$ + CBO | 121.3 |
| | CCC + CBO$^+$ | 121.2 |
| OCCCCB | BCCC + CO | 54.6 |
| | BCC + CCO | 110.6 |
| OCCCCB$^+$ | BCCC$^+$ + CO | 100.6 |
| | BCCC + CO$^+$ | 228.7 |
| | BCC$^+$ + CCO | 255.9 |
| | BCC + CCO$^+$ | 149.8 |

[a] Details of the geometries and energies of [CCCCBO]$^+$ and [OCCCCB]$^+$ are recorded in Table 5 of the Supporting Information, and details of the fragments listed in Table 3 are contained in Table 6 of the Supporting Information.

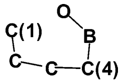
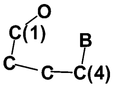
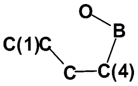
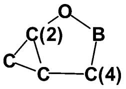
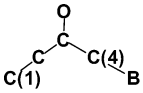
the $^-$CR$^+$ and $^-$NR$^+$ spectra of [CCBO]$^-$ were essentially the same, indicating that neutral CCBO was neither rearranging nor decomposing: the rearrangement peaks (e.g., loss of CO) in these two spectra were coming from [OCCB]$^+$ formed from [CCBO]$^+$.[2] The two spectra shown in Figure 1 are similar, but the peak corresponding to CO loss is reproducibly larger in the $^-$NR$^+$ spectrum. This means that some of the CCCCBO neutrals are rearranging to species which either (i) decompose by loss of CO, or (ii) give cations which lose CO when ionized, or both.[25,26,28]

To determine whether the loss of CO is occurring from a rearranged neutral or by decomposition of the cation formed from that neutral, we need to consider the thermochemistry of decompositions of the neutrals and cations (Table 3). The losses of BO from CCCCBO and CO from OCCCCB are more favorable from energized neutrals than from the corresponding cations. Other fragmentations listed in Table 3 are energetically unfavorable in comparison. The fragmentations of the cations require an extra 69.3 and 45.2 kcal mol$^{-1}$, respectively (Table 3). The data suggest that one-electron oxidation of [CCCCBO]$^-$ produces, in the main, neutrals CCCCBO. However, a minority of the initially formed CCCCBO neutrals have sufficient excess energy to effect rearrangement to OCCCCB, some of which decompose to CCCB and CO.

**3.B. Rearrangement of CCCCBO to OCCCCB: A Theoretical Approach.** As the length of the carbon chain in the $C_n$-BO series increases, the possible number of distinct structural isomers increases dramatically. In the case of the $C_2BO$ system, we considered all possible isomers. In this study we restrict the computed structures to linear neutral molecules (because for $C_2BO$ the linear structures were the more stable isomers[2]), together with any other isomers implicated in the rearrangement of CCCCBO to OCCCCB.[29] These data are listed in Tables 2 and 4. Possible linear structures are shown in Chart 1.

The doublet neutral CCCCBO (**1**) is the global minimum on the neutral potential surface, with OCCCCB (**2**) and OCCBCC (**4**) being only 4.5 and 7.6 kcal mol$^{-1}$ higher in energy than **1**.

**TABLE 4: Geometries and Energies of Transition States (Figure 2) and Reactive Intermediates 7 and 8 (Scheme 2)**

| |  **TS1** |  **TS2** |  **TS3** |  **7** |  **8** |
|---|---|---|---|---|---|
| state | $^2A'$ | $^2A'$ | $^2A'$ | $^2A'$ | $^2A'$ |
| symmetry | $C_s$ | $C_s$ | $C_s$ | $C_s$ | $C_s$ |
| relative energy (kcal mol$^{-1}$)[a] | 53.5 | 44.5 | 116.7 | 66.2 | 139.3 |
| C(1)C(2) (Å) | 1.212 | 1.302 | 1.301 | 1.358 | 1.178 |
| C(2)C(3) (Å) | 1.402 | 1.379 | 1.425 | 1.478 | 1.501 |
| C(3)C(4) (Å) | 1.237 | 1.304 | 1.324 | 1.266 | 1.446 |
| C(4)B (Å) | 1.487 | 1.448 | 1.537 | 1.495 | 1.333 |
| C(1)O (Å) | | 1.235 | | | |
| C(3)O (Å) | | | | | 1.175 |
| BO (Å) | 1.245 | | 1.282 | 1.441 | |
| C(2)O (Å) | | | | 1.341 | |
| C(1)C(2)C(3) (deg) | 106.5 | 82.3 | 149.0 | 63.4 | 179.3 |
| C(2)C(3)C(4) (deg) | 170.0 | 168.1 | 116.2 | 88.9 | 107.1 |
| C(3)C(4)B (deg) | 84.7 | 92.5 | 106.5 | 126.1 | 177.2 |
| C(4)BO (deg) | 162.9 | | 117.0 | 99.3 | |
| C(2)C(1)O (deg) | | 160.8 | | | |
| C(2)C(3)O (deg) | | | | | 124.4 |
| C(2)OB (deg) | | | | 100.3 | |

[a] Energies relative to neutral **1** (−251.611 593 hartrees).

## CHART 1

**CCCCBO** **OCCCCB** **OCCCBC**

**1** ( 0 kcal mol$^{-1}$) **2** (+ 4.5) **3** (+ 50.9)

**OCCBCC** **OCBCCC**

**4** (+ 7.6) **5** (not stable)

Full details of the energies and geometries of these structures are recorded in Table 2. The isomer OCCCBC (**3**) lies 50.9 kcal mol$^{-1}$ above **1**, while CCCBCO (**5**) is not stable at the level of theory used for the calculation. In principle, both of the low-energy isomers **2** and **4** can decompose by loss of CO, but only OCCCCB (**2**) can account for those fragmentations in the $^{-}$NR$^{+}$ spectrum of [CCCCBO]$^{-}$ which do not come from CCCCBO.

What is the mechanism of the rearrangement of CCCCBO to OCCCCB? In the $C_2BO$ system, even though OCCB is only 4 kcal mol$^{-1}$ above CCBO on the neutral potential surface, the barrier to the rhombic transition state separating these structures is 64 kcal mol$^{-1}$, and the rearrangement was not detected experimentally.[2] In the case of the rearrangement CCCCBO to OCCCCB, there are a number of possibilities to consider. These are cyclization processes through six-, five-, and four-center transition structures.

The simplest scenario to consider is the rearrangement through a six-centered state. This rearrangement has been investigated at the MP4SDTQ/aug-cc-pVDZ//MP2(full)/6-31G(d) level of theory, and the results are summarized in Figure 2. Full details of stable species including intermediates are detailed in Table 2, while descriptions of transition structures are given in Table 4. The process shown in Figure 2 is slightly endothermic (+4.5 kcal mol$^{-1}$) and proceeds through the cyclic intermediate **6** (+39.9 kcal mol$^{-1}$) with the system requiring excess energy of ≥ 53.5 kcal mol$^{-1}$ in order to pass the first transition state (cf. 64.0 kcal mol$^{-1}$ for the CCBO rearrangement).[2]

Two other possible mechanisms are shown in Scheme 2. We have not computed the entire reaction coordinates of these two processes. Instead, we have investigated several of the intermediates to show that the two processes are energetically unfavorable in comparison with the six-centered rearrangement shown in Figure 2. Geometries and energies of these key intermediates are recorded in Table 4.

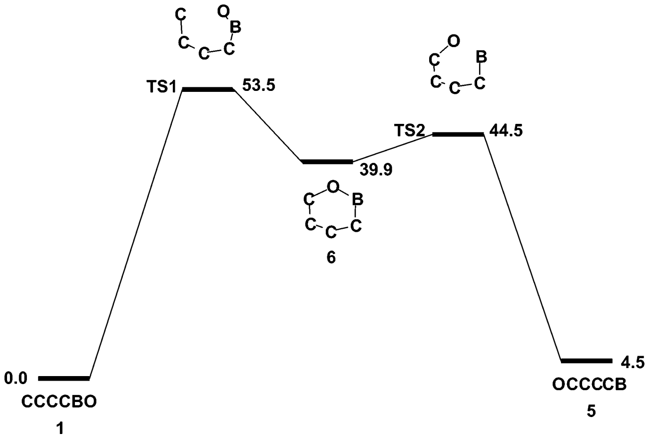
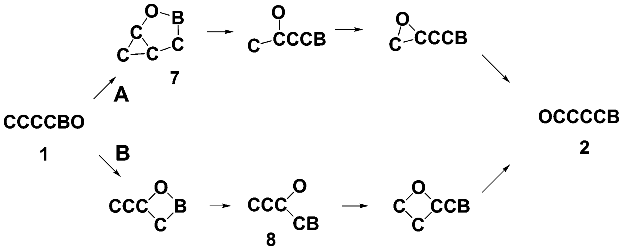


**Figure 2.** Rearrangement of CCCCBO to OCCCCB. Energies are at the MP4SDTQ/aug-cc-pVDZ//MP2(full)/6-31G(d) level of theory. Relative energies are in kcal mol$^{-1}$ with respect to CCCCBO (0 kcal mol$^{-1}$).

## SCHEME 2



Consider first, reaction sequence **A**, which proceeds initially by cyclization through a five-membered transition state. The product of the initial cyclization is the unusual bicyclic species **7**, which lies 66 kcal mol$^{-1}$ above CCCCBO (**1**). The barrier for the first step from **1** to **7** is 116.7 kcal mol$^{-1}$. This process requires significantly more energy than that required for the process shown in Figure 2 and is not considered further. Sequence **B** is even less favorable. Key intermediate **8** lies 140 kcal mol$^{-1}$ above **1**, an energy requirement 86.5 kcal mol$^{-1}$ higher than that required to effect the rearrangement shown in Figure 2.

## 4. Conclusion

(a) One-electron vertical oxidation of [CCCCBO]$^-$ forms the doublet CCCCBO. The majority of these neutrals are stable at least for the microsecond duration of the NR experiment.

(b) A minority of neutrals CCCCBO species (formed as indicated above) are energized and rearrange via a six-center cyclization, involving O−C(1)bond formation followed by B−O bond cleavage to form OCCCCB. This reaction is endothermic by only 4.5 kcal mol$^{-1}$ but requires excess energy of $\geq$ 53.5 kcal mol$^{-1}$ in order to surmount the first transition state. This energy requirement is 45.5 kcal mol$^{-1}$ more than the Franck−Condon excess energy of 8 kcal mol$^{-1}$ of CCCCBO produced by the vertical oxidation process. This additional energy may be produced by keV collisions of CCCCBO with the collision gas following Franck−Condon neutralization of [CCCCBO]$^-$. Alternatively, a minority of the CCCCBO neutrals may have sufficient excess energy (to cause rearrangement) as a consequence of the collision-induced Franck−Condon oxidation itself.

(c) The earlier report that CCBO is stable under the NR conditions[2] is consistent with the observation in this study that some CCCCBO neutrals rearrange under the same experimental conditions. Neutral CCCCBO rearranges to OCCCCB via a six-center transition state, a process not available to CCBO.

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**Supporting Information Available:** Details of the energies and geometries of the cations [CCCCBO]$^+$ and [OCCCCB]$^+$ and details of the energies of all the fragment species listed in Table 2. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Van Orden, A.; Saykally, R. J. *Chem. Rev.* **1998**, *98*, 2313.

(2) McAnoy, A. M.; Dua, S.; Schröder, D.; Bowie, J. H.; Schwarz. H. *J. Phys. Chem. A* **2003**, *107*, 1181 and references therein.

(3) Zhan, C. G.; Iwata, S. *J. Phys. Chem.* **1997**, *101* (1) 591.

(4) Hamrick, Y. M.; VanZee, R. J.; Godbout, J. T.; Weltner, W. J.; Lauderdale, W. J.; Stanton, J. F.; Bartlett, R. J. *J. Phys. Chem*. **1991**, *95*, 2840.

(5) Burkholder, T. R.; Andrews, L. *J. Phys. Chem*. **1992**, *96*, 10195.

(6) Wang, C.; Huang, R.; Liu, Z.; Zheng, L. *Chem. Phys. Lett.* **1995**, *242*, 355.

(7) Zhou, M.; Tsumori, N.; Li, Z.; Fan, K.; Andrews, A.; Xu, Q. *J. Am. Chem. Soc*. **2002**, *124*, 12936−12942.

(8) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485.

(9) Schalley, C. A.; Hornung, G.; Schröder, D.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1998**, *172*, 181; *Chem. Soc. Rev.* **1998**, *27*, 91.

(10) Zagorevskii, D. V.; Holmes, J. L. *Mass Spectrom. Rev.* **1999**, *18*, 87.

(11) Blanksby, S. J.; Schröder, D.; Dua, S.; Bowie, J. H.; Schwarz, H. *J. Am. Chem. Soc.* **2000**, *122*, 7105.

(12) DePuy, C. H.; Bierbaum, V.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Smitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

(13) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

(14) (a) Bowie, J. H.; Blumenthal, T. *J. Am. Chem. Soc.* **1975**, *97*, 2959. (b) Szulejko, J. E.; Bowie, J. H.; Howe, I.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 99.

(15) Bursey, M. *Mass Spectrom. Rev.* **1990**, *9*, 555.

(16) Hornung, G.; Schalley, C. A.; Dieterle, M.; Schröder, D.; Schwarz, H. *Chem.*−*Eur. J.* **1997**, *3*, 1866.

(17) Schalley, C. A.; Blanksby, S. J.; Harvey, J. N.; Schröder, D.; Zummack, W.; Bowie, J. H.; Schwarz, H. *Eur. J. Org. Chem*. **1998**, 987.

(18) Brown, H. C.; Bhat, N. G.; Srebnik, M. *Tetrahedron Lett*. **1988**, *29*, 2631.

(19) Brown, C. D.; Chong, J. M.; Shen, L. *Tetrahedron* **1999**, *55*, 14233.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) Scott, A. P.; Radom, L. *J. Phys. Chem*. **1996**, *100*, 16502.

(22) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(23) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

(24) A reviewer has asked us to comment on the accuracy of the calculations, in particular, the applicability of diffuse functions. The level of theory used in this study is the same as that used in previous studies (e.g., ref 2). The level of theory is not perfect but is used as a guide to rationalize the experimental findings. Addition of diffuse functions makes little difference in the geometries of neutrals, but they are important for the determination of energies. This is the approach taken in this study.

(25) A reviewer has suggested that since the process CCCCBO → CCCC + BO is endothermic by 29.8 kcal mol$^{-1}$ (see Table 3) [cf. the rearrangement CCCCBO → OCCCCB, which is endothermic by 4.5 kcal mol$^{-1}$ but has a barrier of 53.5 kcal mol$^{-1}$ (see Figure 2)], the decomposition may be more feasible than the rearrangement. However, this cleavage reaction is unlikely to be barrierless, since the $C_2C_3$ bond distances are appreciably different between CCCC and CCCCBO (see Tables 3 and 6).

(26) A reviewer has asked us to comment on the possibility of both synchronous and stepwise removal of two electrons in the $^-$CR$^+$ process. Following the first reports of $^-$CR$^+$ processes,[14] it was pointed out[15,27] that two-electron removal could be stepwise. This matter has been dealt with in full recently.[9] In summary, a $^-$CR$^+$ spectrum always reflects a superimposition of 1 × 2e and 2 × 1e processes. However, the collision cross section for CR is always at least a factor of 5 (in the particular case dealt with in this paper closer to 100) larger than the cross section for NR. Thus, any interference with $^-$NR$^+$ processes in $^-$CR$^+$ is minimal. The key features to be considered in a comparison of the two spectra are differences between the spectra and what those differences imply.

(27) Clair, R.; Holmes, J. L.; Mommers, A. A.; Burgers, P. C. *Org. Mass Spectrom.* **1985**, *20*, 207.

(28) A reviewer has pointed out that although the loss of CO is more pronounced in the $^-$NR$^+$ spectrum (supporting the proposal of rearrangement of CCCCBO to OCCCCB), the CCB$^+$ ($m/z$ 35) to CCC$^{+\bullet}$ ($m/z$ 36) peak ratio in the $^-$NR$^+$ spectrum appears to be in the wrong direction. This is a subtle issue. If neutral CCCCBO fragments to yield equal amounts of CCC and CBO (see Table 3), it might be assumed that, since the ionization energies of CCC and CBO are very similar (see Table 3), the peaks corresponding to the two product cations should be formed in equal abundance. However, the reionization cross section of CCC is higher than that of CBO, since the geometries of CCC and CCC$^{+\bullet}$ are very similar, while those of CBO and CBO$^{+\bullet}$ are significantly different (see Table 6). The overall consequence is that the peak for CCC$^{+\bullet}$ in the $^-$NR$^+$ spectrum is larger than that in the $^-$CR$^+$ spectrum.

(29) There is a cyclic isomer which is more stable than CCCCBO, but it is not involved in the rearrangement of CCCCBO to OCCCCB. This is the (rhombic $C_4$)-BO structure [$^2B_1$ state, 5.4 kcal mol$^{-1}$ below CCCCBO at the MP4 SDTQ/aug-cc-pVDZ//MP2(full)/6-31G(d) level of theory]. The rhombic $C_4$ portion of this structure is very similar to that of rhombic $C_4$ reported earlier.[11] The (rhombic $C_4$)-BO structure has $C_{2v}$ geometry: bond lengths (Å); $C_1C_2$ (1.439), $C_2C_3$ (1.528), $C_3C_4$ (1.417), BO (1.220); bond angles (deg); $C_1C_2C_3$ (57.9), $C_2C_3C_4$ (57.4), $C_3C_4B$ (147.4), and $C_4BO$ (180.0).